Breaking the Gibbs Adsorption Rule in Liquid Metals

Beamline: X25

Technique: Resonant X-ray Reflectivity from a Liquid Surface

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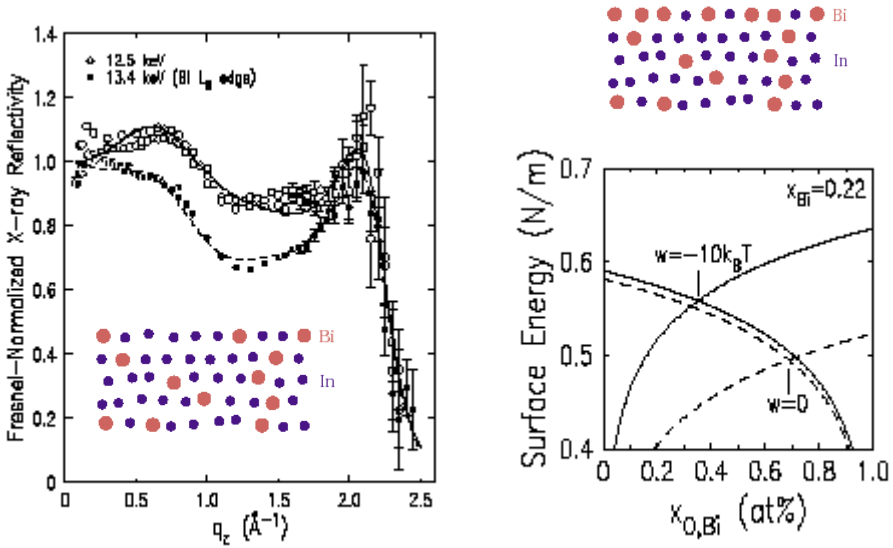
E. DiMasi et al. "Pairing Interactions and Gibbs Adsorption at the Liquid Bi-In Interface: Observations by Resonant X-ray Reflectivity." *Phys. Rev. Lett.*, 86 (2001) 1538.

Motivation: Binary liquids are supposed to follow a simple rule, formulated by Gibbs in 1878: the lowest surface tension species segregates at the surface. This picture assumes that interactions between atoms can be disregarded. What happens in liquids with attractive interactions? To answer this question, we performed resonant x-ray reflectivity measurements from a liquid 22% Bismuth – 78% Indium alloy. By tuning the incident x-ray energy through the Bi LIII absorption edge, we determined the ratio of Bi to In at the surface. The Gibbs prediction is 70% Bi for the non-interacting system.



Left: X-ray reflectivity from the liquid Bi-In surface as x-ray energy is varied near the Bi LIII edge. Inset schematically shows the observed surface segregation of 35 at% Bi. Right: in the absence of attractive interactions, predicted Bi enrichment is 70%. Attractive interactions must be of order $10k_BT$ to explain the observations.

Results: We find a Bi enrichment of 35 at% in the surface layer, compared to the 22 at% in the bulk. This is considerably less Bi than would be expected in the absence of attractive Bi-In interactions, which we find must be on the order of 10 k_BT to explain our data. This work quantifies, for the first time, the extent to which attractive interactions can compete with Gibbs adsorption. These are the first resonant x-ray reflectivity measurements ever achieved on a liquid surface, and were made possible by specialized instrumentation at the National Synchrotron Light Source at BNL.